

National Occupational Health and Safety Commission

**ARSENIC AND ITS
COMPOUNDS**

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The National Commission's address is:

National Occupational Health and Safety Commission
Level 30, St Martins Tower
31 Market Street
Sydney NSW 2000
GPO Box 58
Sydney NSW 2001
Tel: (02) 265 7555
Facsimile: (02) 265 7538
Telex: 177243

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Foreword

The National Occupational Health and Safety Commission, Worksafe Australia, is a tripartite body established by the Commonwealth Government to develop, facilitate and implement a national approach to occupational health and safety.

The National Commission comprises representatives of the peak employee and employer bodies - the Australian Council of Trade Unions (ACTU) and Confederation of Australian Industry (CAI) - as well as the Commonwealth, State and Territory governments.

Since its establishment, the National Commission has produced occupational health guides. Before the National Commission was established, a series of similar guides was published by the National Health and Medical Research Council.

This Guide has been reviewed and endorsed by a working group of the National Commission as part of the co-ordinated effort by the Commonwealth, State and Territory governments and employee and employer organisations to make Australian workplaces safe and healthy.

Although this Guide has been endorsed by the National Commission, it is an advisory document only. It is produced and distributed in the interests of providing useful information on occupational health and safety for employers, employees and others. This document does not replace statutory requirements under relevant State and Territory legislation.

This Guide is aimed primarily at workers and managers but should also be useful to occupational health and safety personnel and others. It may be used in conjunction with appropriate training and consultation, in line with good management practice.

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Introduction

This Guide outlines some of the potential health hazards associated with the use of arsenic and its compounds.

For particular application, this Guide should be read in conjunction with the following Worksafe Australia Guides:

- *Electroplating*; and
- *Atmospheric Contaminants*.

The National Commission publication, *Exposure Standards for Atmospheric Contaminants in the Occupational Environment* (latest edition), should also be consulted for the latest standard for the maximum allowable airborne exposure to arsenic.

Reference should be made to the manufacturer's specific product information in the form of a material safety data sheet (MSDS) for particular products which contain arsenic. The MSDS should be updated regularly. MSDS should conform to the National Commission's recommended format and should be freely accessible to all personnel.

Identification

Arsenic and its compounds

Arsenic is present in all soils, and in many parts of the world it appears in drinking water obtained from wells drilled into arsenic-rich ground strata. It is commonly found in association with coal, gold, nickel, cobalt, antimony and iron ores and as arsenides or sulphides in copper, lead and zinc sulphide ores in proportions ranging from parts per million to 15 per cent.

Arsenic is present in sea water and the total daily intake of arsenic varies according to the amount of seafood in the diet. Other, possibly important, non-occupational sources of arsenic are the drinking of contaminated bore and well water, eating sprayed fruit and vegetables, burning wood treated with arsenic, taking medicinal arsenicals and smoking contaminated tobacco.

Sources of occupational exposures to arsenic may include:

- **Mining and processing:** Arsenic is a constituent of many alloys, including those of copper, lead, zinc, silver and germanium. It is alloyed with lead in making, for example, lead shot, lead-based bearing metals and battery grids. Arsenic is often removed as an impurity during the smelting of copper, lead and zinc.
- **Wood preservation:** Wood fibres are impregnated under pressure with copper chrome arsenate.
- **Herbicide:** Monosodium methyl arsenate, disodium methyl arsenate and sodium arsenate are used extensively in agriculture.
- **Pesticide:** Lead arsenate is used to some extent in horticulture. Arsenic trioxide is used in termite control.
- **Glass making:** Arsenic trioxide and pentoxide are used to produce clear glass, free from the green stain of iron impurity.
- **Hide preservation:** Arsenic trioxide and sodium arsenite are used as hide preservatives.
- **Food additive:** Derivatives of phenylarsenic acid are added to fowl and pig feed.
- **Laboratory procedures:** Arsenic trichloride is used in organo-arsenic chemistry and in chemical analysis procedures.

Arsine is a highly poisonous and flammable gas. The following discussion of arsenic and its compounds is relevant to arsine. Any specific or additional considerations needed with arsine is discussed in the section following arsenic.

Health Hazards

When considering the hazards associated with any workplace, it is essential to understand the relationship between 'hazard', 'exposure' and 'risk'.

'Hazard' is the potential for an agent or process to do harm. 'Risk' is the likelihood that an agent will produce injury or disease under specified conditions.

Health effects can only occur if a worker is actually exposed to the hazard. The risk of injury or disease usually increases with the duration and frequency of exposure to the agent, and the intensity/concentration and toxicity of the agent.

Toxicity refers to the capacity of an agent to produce disease or injury. The evaluation of toxicity takes into account the route of exposure and the actual concentration of an agent in the body.

Exposure to hazardous material may be acute or chronic. *Acute exposures* generally refer to single dose, high concentration exposures over short periods, while *chronic exposures* involve repeated or continuous exposures over long periods. These exposures may have acute, immediate effects or chronic, long term effects.

Exposure routes

Routes of entry by which harmful substances enter the body at work are by inhalation, absorption and ingestion.

- *Inhalation* is the most significant route of entry by which harmful substances enter the human body at work. Many occupational diseases caused by chemicals result from breathing air that contains harmful substances.
- Some substances may be *absorbed* through the skin. This can occur without any noticeable change to the skin, or with evidence of damage to the skin, depending on the substance.
- *Ingestion* is of relatively minor significance in occupational exposure to toxic materials.

The most common hazards of occupational exposure to arsenic compounds are:

- Irritation of the skin, eyes, mouth, throat and lungs.
- Chronic poisoning, including cancer of the skin and lungs.
- Acute poisoning that may result in death. Acute poisoning by arsenic compounds other than arsine rarely occurs in industry but has been reported to have occurred as a result of inhalation and skin absorption as well as from ingestion.

In the workplace, absorption of arsenic compounds occurs primarily through the lungs following inhalation of airborne arsenic fumes or dusts. In addition, arsenic compounds may be absorbed from the gastro-intestinal tract and some arsenic compounds, for example, arsenic acid and arsenic trichloride, may be absorbed through the skin.

Soluble compounds of arsenic, for example, sodium arsenite, are more toxic than insoluble compounds, for example, arsenic sulfide. Trivalent compounds, for example, arsenic trioxide and arsenic trichloride are generally more toxic than pentavalent compounds, for example, arsenic pentoxide. Organic arsenic compounds are generally much less toxic than inorganic compounds.

Health effects

Irritant effects

Arsenic trioxide dust may cause dermatitis of the face and eyelids and conjunctivitis. In the presence of sweat, skin abrasions, chafing or wounds, arsenic readily promotes ulceration of the skin. Dermatitis, with scaling and excessive pigmentation of the skin, has occurred among workers manufacturing insecticides, in vineyard workers and unprotected smelter workers. Exposure to arsenic trichloride has also produced blistering of the skin. Irritation of the nose, throat and lungs, impaired respiration and perforation of the nasal septum have also been reported in smelter workers.

Systemic toxicity

Chronic arsenic poisoning due to exposure to compounds such as calcium arsenate and copper acetoarsenate, is characterised by weakness, loss of appetite, gastro-intestinal disturbances, numbness and tingling of the extremities (peripheral neuritis). Chronic exposure to arsenic compounds, such as arsenic trioxide, may lead to liver damage and skin disorders such as keratoses and pigmentation.

Cancer

Recent studies have shown that arsenic and its compounds can cause cancer in humans. Exposure to inorganic arsenic compounds in drugs and the occupational environment is causally associated with the development of skin cancer. Exposure to arsenic compounds has also been associated with increases in the incidence of various other types of cancers, particularly cancer of the lung among copper smelter and pesticide workers.

Prevention and Control Measures

Following the identification of a hazard, evaluation of work practices and conditions must be undertaken so that effective prevention and control measures can be implemented. This should be considered an integral part of management's responsibilities.

Evaluation

Environmental sampling and analysis should be undertaken at regular intervals by qualified occupational health and safety professionals in accordance with the methods recommended by the appropriate occupational health authority. (Refer to National Institute of Occupational Safety and Health, *Manual of Analytical Methods*, vol. 1, 3rd Edition, National Institute of Occupational Safety and Health, Cincinnati, 1984 for an example of the methods used).

Monitoring

Monitoring may be used for the evaluation of a hazard and for assessing the effectiveness of control measures. The design and implementation of a monitoring program should be carried out by, or in consultation with, a properly qualified person with an adequate knowledge of:

- the objective of the assessment;
- the correct way of using instruments and their limitations;
- the analysis, interpretation and recording of results; and
- the normal operating conditions of the workplace.

Monitoring of the work environment involves the measurement of atmospheric contaminants at selected locations in the workplace (static, positional monitoring). Personal monitoring involves the measurement of atmospheric contaminants in the breathing zone of the individual worker. Biological monitoring involves measurement of the concentration of a contaminant, its metabolites or other indicators in the tissues or body fluids of the worker. In some cases, biological monitoring may be required to supplement static or personal monitoring.

In the control of health hazards due to a specific contaminant, where it has been demonstrated that the exposure of the employee to the contaminant

- is approaching the exposure standard of 0.05 mg/m³ (as As), or
- where biological monitoring indicates that an unacceptable exposure is occurring such that the average urinary excretion exceeds 220 micrograms of arsenic per gram of creatinine,

immediate action must be taken to reduce the health hazard and intensive monitoring should continue.

Records of the results of any monitoring should be maintained. Records should include the following information:

- when the monitoring was done and what the results were;
- what monitoring procedures were adopted, including the duration;
- the location where samples were taken and the specific operations in progress at the time and, in the case of personal samples, the names of workers concerned; and
- what preventive and remedial action was subsequently taken.

Results of personal monitoring are confidential and should be communicated to individual employees. The overall air monitoring results should be available for inspection by personnel working in the areas where arsenic may be present. All air monitoring records should be kept and maintained by employers for a period of not less than 30 years.

Biological monitoring

For evaluation of occupational exposure to arsenic, urine sampling may prove to be adequate. Urinary arsenic levels in persons exposed to arsenic are a useful index of exposure and absorption, but are not of much value as diagnostic aids in individual cases of arsenic poisoning. The majority of unexposed persons have urinary arsenic levels less than 0.1 mg/L unless there is a history of specific arsenic intake, such as from pharmaceuticals or seafoods.

Hair and liver analysis is considered to be of diagnostic value, however, the significance of arsenic in hair often is obscured owing to the difficulty in distinguishing externally deposited arsenic from systemically absorbed arsenic in the hair.

Information concerning the metabolism and excretion of arsenic and the use of biological tests is provided in Appendix 2.

Exposure standards

Arsenic and its compounds are established human carcinogens. (**Note: Arsine has not been shown to be a human carcinogen.**) There is sufficient evidence to establish a causal association between human exposure to these substances and the development of cancer.

Under these conditions, the use of arsenic should be controlled to the highest workable standard by the application of effective engineering control techniques and, where necessary, complemented by the use of appropriate personal protective equipment. Routine monitoring of the workplace is essential for indication of control performance. In some cases, health surveillance and biological monitoring can indicate exposure, thus revealing the need for reassessment of the control measures and work practices.

Worker exposure to arsenic and its compounds should be kept as low as workable. Every attempt should be made to keep exposures well below the exposure standard given in the 1990 edition of the National Commission publication, *Exposure Standards for Atmospheric Contaminants in the Occupational Environment*. The eight-hour time-weighted average exposure standard for arsenic and its compounds is given as:

arsenic and its compounds (as As) - 0.05 mg/m³

The most recent edition of *Exposure Standards for Atmospheric Contaminants in the Occupational Environment* must always be consulted for current values.

Even though the eight-hour time-weighted average exposure standard is not exceeded, it is not desirable to expose employees to concentrations higher than the exposure standard solely because the exposure lasts for less than an eight-hour day or because the exposure occurs only occasionally. Any excursion above the time-weighted average exposure standard should be restricted in accordance with the recommendations detailed in the exposure standards document.

The exposure standards do not represent 'no effect' levels which guarantee protection to every worker.

Control measures

Where there is a likelihood of worker exposure to arsenic compounds, steps should be taken to minimise that exposure as far as workable. A thorough examination of work practices is essential. Procedures should be adopted to ensure that workers are not unnecessarily exposed to the hazard. Control measures include, but are not limited to, the following, which are ranked in priority of their

effectiveness:

- elimination/substitution and process modification;
- engineering controls;
- administrative controls; and
- use of personal protective equipment.

Engineering controls

Care in selection, design, installation, operation and regular maintenance is essential to ensure that the system adequately controls contamination at all times.

The design of an effective ventilation system is a highly specialised area of expertise and therefore should be performed only by those competent to do so. Special care in design is important where combustible, inflammable or potentially explosive materials are involved. Inlets and outlets must not be blocked and must be kept clear at all times.

Air from a local exhaust ventilation system should not be recirculated into the workroom. It should be discharged to the outside air, distant from other work areas, air conditioning inlets or compressors supplying breathing air.

General ventilation systems are not usually as satisfactory in the control of health hazards as is the use of ventilated process enclosures or local exhaust ventilation, but they may be useful to control minor emissions of contaminants of low toxicity. In designing a mechanical ventilation system where such contamination occurs, particular attention should be given to fan selection and to the placement of air extractors and fresh air supply openings. In particular, movement of air should be arranged so that clean air streams are drawn past workers and contaminated ones lead away from them. Such systems require rigorous control over all sources of natural ventilation and air movement which may disturb planned air movement, for example, the operation of air conditioning systems or the opening and closing of doors and windows. Changes or additions to a balanced ventilation system must be implemented in such a way that they will not result in reduced efficiency of the entire ventilation system.

Breathing apparatus should be used only where ventilation or engineering control is impracticable or in non-routine situations.

Incompatibilities

Arsenic compounds may liberate arsine when exposed to strong reducing conditions. Such conditions are usually produced by hydrogen released by the action of inorganic acids on metals.

Other examples of incompatibilities are listed below:

- Arsenic trioxide filings will explode on heating.
- Arsenic trichloride produces hydrogen chloride when in contact with water.
- In most cases where arsine can be formed, stibine (SbH_3), another toxic gas, can also be formed if antimony is present. Stibine is similar to arsine in toxicity and causes a specific toxic action which closely resembles that of arsine.

Personal protective equipment

In certain circumstances, such as in the smelting of arsenical ores, cleaning of flues and dust collectors, in the loading and transport of arsenic trioxide and repairing and cleaning of furnaces, personal protection of the individual may be required as a supplement to other preventive action. It should not be regarded as a substitute for other control measures and must only be used in conjunction with substitution and elimination measures.

Personal protective equipment must be appropriately selected, individually fitted and workers trained in their correct use and maintenance. Personal protective equipment must be regularly checked and maintained to ensure that the worker is being protected. Refer to Australian Standard AS 1715 for further details.

The following protective clothing and equipment should be provided:

- Coveralls or similar full-body work clothing.
- PVC or rubber gloves, and shoes or coverlets.
- Impervious gloves, aprons and face shields or splash goggles where liquids are being processed in a manner that may result in splashes.
- Impervious clothing for employees subject to exposure to arsenic trichloride.
- Appropriate respiratory protective equipment for the concentration of arsenic that may be in the air. As the concentration of arsenic increases, respiratory protective equipment with a higher protection factor should be used. The respiratory protective equipment used should be in accordance with Australian Standard AS 1716.

Environmental and personal hygiene

Employees should have ready access to clean work clothes, protective clothing, change rooms, showers and adequate washing and laundry facilities. Splashes by irritant or sensitising substances must be washed off immediately with soap and water. Contaminated clothing must be removed.

Protective clothing should be laundered at least weekly. Work clothing should not be taken home. It should be laundered on the premises or by a commercial laundry which has been informed of the hazards.

Handle gloves and other protective equipment carefully and safely. Wash after use.

Do not store respiratory equipment, clothing or protective equipment where arsenic is stored or used.

Cleaning of walls, floors, ceilings, overhead structures, windows, tables, ledges, machinery and other equipment should be effected either by vacuum cleaning using cleaners fitted with High Efficiency Particulate Air (HEPA) filters for removing hazardous particles or by wet methods. HEPA filters must comply with the 99.97 per cent minimum efficiency requirement of Australian Standard AS 1324, section 4.3.1. Dry sweeping or blowing is not acceptable. Whenever the nature of the work requires it, floors, benches or tables should be covered with an impervious material which can be hosed or wetted easily.

Any spills should be cleaned up promptly. MSDS should be consulted because in some cases specific cleaning methods or materials may be necessary. Waste materials should be removed and disposed of by methods suitable to the type of hazards that may be produced.

Do not eat, drink, smoke or keep food, drink, utensils or cigarettes where arsenic is stored or used.

Hands and face must be washed before eating, drinking, smoking and going to the toilet. Washing facilities must be provided for this purpose.

Where work is to be conducted in a confined space, work practices should be in accordance with Australian Standard AS 2865.

Examine any task undertaken by operators or maintenance personnel for the possibility of arsine formation.

Metal dross liable to contain arsenic should be rendered inactive by roasting it with sawdust for at least one hour at 980°C and any gases produced vented safely.

The removal of potentially arsenic-containing sludges from tanks should be done by power hosing which should be directed from a position outside the tank. When entry is necessary, all the precautions appropriate for entry into a confined space should be taken, including the use of a life-line and a supplied air respirator. Specific precautions should include the use of non-metallic implements such as spades, scrapers and plastic buckets.

All surfaces should be maintained as free as possible of accumulations of arsenic.

Arsenic should be removed from work areas by vacuum cleaning with approved equipment or by wet methods. Cleaning may be performed by washing down with a hose, provided that a fine spray of water has first been laid down. Sweeping, or the use of other methods which can stir dust, should be considered only where the above is impractical and with the appropriate controls to minimise associated risks.

Cleaning equipment should be used and emptied in a manner which minimises the re-entry of arsenic into the workplace.

Dust collection and ventilation equipment should periodically be cleaned and checked for effectiveness.

Note: For information on the disposal of arsenic containing wastes and the washings from cleaning procedures, refer to the section on disposal.

Health assessment

In some occupations, health assessment may form part of a comprehensive occupational health and safety strategy. Where employees are to undergo health assessment, there should be adequate consultation prior to the introduction of any such program. It is particularly valuable to be able to relate employee health and illness data to exposure levels in the workplace. Medical records must be confidential.

Medical surveillance is necessary for persons exposed to arsenic. A skin examination should be carried out, with any abnormalities noted and acted on as necessary. A urine sample should be taken for determination of urinary arsenic levels.

Education and training

All employees working with arsenic compounds must be informed of the hazards from exposure to the contaminant and the precautions necessary to prevent damage to their health. Employees should be trained in appropriate procedures to ensure that they carry out their work so that as little contamination as possible is produced, and in the importance of the proper use of all safeguards against exposure to themselves and their fellow workers. Adequate training in the proper execution of the task and in the use of all associated engineering controls, and of any personal protective equipment, is essential.

Employees exposed to contamination hazards should be educated in the need for, and proper use of, facilities, clothing and equipment and thereby maintain a high standard of personal cleanliness. Special attention should be given to ensuring that all personnel understand instructions, especially newly recruited employees and those with English-language difficulties, where they are known.

Before handling any materials, MSDS should be obtained from the suppliers.

A management representative should be nominated as responsible for the supply and maintenance of, and training in, personal protective equipment.

Ensure that all personnel understand the safety procedures associated with the storage and handling of arsenic. This should include a program on the use and maintenance of respiratory protective equipment.

Ensure that all personnel are informed of the toxicity of arsenic and the symptoms and signs of arsine poisoning and of the need to seek proper medical attention for all cuts, scratches and other injuries. A notice of action to be taken in case of suspected poisoning should be displayed in a prominent place in all areas where arsenic is handled and stored and in the first aid station.

Ensure that all personnel have a knowledge of the procedures to be followed in case of a fire, spill or leak.

Signs

Tanks, pipelines and supply valves should be clearly labelled in appropriate languages, in accordance with the provisions of Australian Standard AS 1319. Labels should indicate, where appropriate, the nature of the contents, the strength and temperature and also the nature of the hazard and its emergency treatment.

Storage

Arsenic compounds should be stored in cool, dry, well-ventilated areas. Containers should be kept tightly closed to protect from atmospheric moisture and away from water, acids, heat and direct sunlight.

Fire

On heating, arsenic compounds produce toxic fumes.

In case of fire where arsenic is stored or used:

- move people upwind from the area;
- contact the fire brigade;
- wear self-contained breathing apparatus and full protective clothing, including boots;
- if safe to do so, move containers from the fire area;
- for small fires, use dry chemical, carbon dioxide, water spray or foam;
- for large fires, use water spray, fog or foam. (In cases where arsine gas may be produced by heat only, use water spray or fog with extreme caution.); and
- prevent water run-off from entering drains, waterways or water storages.

Spills or leaks

If there is a spill of an arsenic compound, the following precautions should be observed:

- do not enter the area unless wearing self-contained breathing apparatus, full protective clothing, including boots, PVC or rubber gloves and chemical goggles to prevent contact with eyes and skin;
- personnel protective equipment must be worn should any attempt be made to close off the source of the spill or leak;
- evacuate the area and move upwind to avoid inhalation of vapour and contact with skin and eyes;
- depending on the size and location of the spill, notify the fire brigade, police and/or emergency contact;
- smoking, naked lights or ignition sources should not be permitted;

- collect the spilled material and place it in a clean, labelled and sealable container for later disposal. (If using a metal container, ensure that it is not incompatible with the arsenic compound to be disposed of.);
- absorb liquid forms of arsenic with sand or other non-combustible absorbent material; and
- do not allow the spillage to enter drains, waterways or water storage.

In addition to the above general precautions, the following measures should be taken for large spills or leaks:

- evacuate the area and move upwind to avoid inhalation of vapour and contact with skin and eyes;
- ventilate closed spaces before entering; and
- do not wash away with water.

For additional precautions with arsine spills and leaks, refer to the separate section on arsine.

Disposal

Waste material must be disposed of in a manner that will prevent exposure of humans and animals as well as pollution of air and water. The appropriate toxic waste disposal authority in the State or Territory should be contacted before disposal of arsenic containing wastes and the washings from cleaning procedures.

First Aid

Wherever there is a possibility of eye contamination, emergency eyewash facilities should be provided within the immediate work area.

Wherever there is any possibility of skin exposure, deluge showers and washing facilities should be provided.

In the case of acute exposure to arsenic compounds:

- move the victim to fresh air;
- if breathing is difficult, give oxygen;
- if not breathing, give artificial respiration;
- in case of skin or eye contact with material, immediately flush the skin or eyes with running water thoroughly;
- remove and isolate contaminated clothing and shoes;
- keep the victim quiet and warm; and
- obtain advice from a doctor or poisons information centre.

Note: Since effects may be delayed, keep the victim under observation.

Arsine

Arsine (AsH_3) is a highly poisonous and flammable gas. Commercially produced arsine has only limited industrial use in the manufacture of electronic components and in organic synthesis. However, under certain circumstances, arsine may be produced accidentally from arsenic compounds or materials containing arsenic as contaminants and cause unexpected poisoning.

The gas is colourless, heavier than air, non-irritating but highly poisonous. It has a mild garlic odour but this does not provide a reliable warning.

Early recognition of arsine poisoning is very important and requires an awareness of the circumstances which may lead to hazardous exposure to this gas, such as the reaction of metallic arsenic with acids. Further examples are listed in Appendix 1.

Arsine toxicity

Workers poisoned by arsine usually complain of bloodstained urine, stomach cramps and nausea. There is usually a delay of two to 24 hours before the onset of headache, malaise, weakness, dizziness, difficult breathing, abdominal pain, nausea and vomiting which, depending on the severity of exposure, may rapidly progress to severe illness with vomiting, intense headache and pains in the loins.

In such cases:

- bloody urine, light to dark red, is noticed four to six hours after exposure to arsine;
- there is a progressive reduction in the amount of urine formed and, possibly, complete failure of kidney function within a few days;
- jaundice is usually evident on the second or third day; and
- arsine is broken down to an organic compound of arsenic in the blood stream and evidence of arsenical poisoning of the nervous system may be observed after several days.

The presentation of such symptoms requires immediate investigation as fatalities may occur.

The effects of inhalation of arsine gas in humans are indicated in the following table:

Concentration	Effects of Inhalation
10 ppm (32 mg/m ³)	lethal after longer exposures
10 ppm (32 mg/m ³)	lethal after longer exposures
25-50 ppm (80-160 mg/m ³)	exposure for half an hour is fatal
250 ppm (800 mg/m ³)	immediately fatal

Exposure standards

Worker exposure to arsine should be kept as low as workable. Every attempt should be made to keep exposures well below the exposure standard of 0.2mg/m³, 0.05 ppm.

The exposure standards represent airborne concentrations of individual chemical substances which, according to current knowledge, should neither impair the health of, nor cause undue discomfort to, nearly all workers. Additionally, the exposure standards are believed to guard against narcosis or irritation which could precipitate industrial accidents.

Except where modified by consideration of excursion limits, exposure standards apply to long term exposure to a substance over an eight-hour day for a normal working week, over an entire working life.

The exposure standards do not represent 'no effect' levels which guarantee protection to every worker.

Ventilation

Arsine is particularly hazardous when in a confined space, for example, in a tank, vat, boiler, sewer, ship or silo. Procedures for working in confined spaces should be established in accordance with Australian Standard AS 2865 and relevant State and Territory requirements.

Incompatibilities

Examples of incompatibilities are listed below:

- arsine can react vigorously with oxidising materials, for example, bromates, chlorates, iodates and peroxides; and
- arsine may explode when exposed to chlorine, nitric acid or potassium plus ammonia.

Fire

Arsine gas cylinders should be stored away from heat and sparks.

Arsine is extremely flammable and may be ignited by heat, sparks or flames. Vapours may travel to a source of ignition and flash back. They can form explosive mixtures with air and oxidising agents.

In case of fire in locations where arsine is stored, cool containers with water until well after the fire is out because they may explode.

Where arsine is on fire:

- if safe to do so, let the fire burn; and
- only use water spray or fog with great caution as its use to prevent ignition or control flame propagation of flammable gases or vapours may be extremely dangerous.

Spills or leaks

For small spills or leaks of arsine:

- evacuate the area; and
- force ventilate.

For large spills or leaks of arsine:

- evacuate the area and move upwind;
- wear positive-pressure breathing apparatus and full protective clothing (powered air purifying devices are not suitable);
- remove sources of ignition; and
- use water spray to reduce vapours.

First aid

The outlined first aid procedure for arsenic and its compounds also applies to arsine exposure.

Appendix 1

Arsine production in industry

Arsine produced by the hydrolysis of metallic arsenides in the smelting and refining of metals has been the cause of most reported cases of arsine poisoning. Two examples of arsine produced in this way are listed below.

- In silicon steel production, aluminium added during the pouring stage combines with arsenic, originally present in the iron ore, and collects in the dross. Any subsequent wetting of the dross can cause the generation of hydrogen which reacts with the combined arsenic to form arsine.
- Lead alloys used in car battery manufacture may contain calcium as a hardener and arsenic as a corrosion inhibitor. During recycling, the remelting of lead battery scrap results in the combination of arsenic and calcium to form calcium arsenide which collects in the dross. Any subsequent wetting of the dross causes the release of arsine.

When arsenic is present as a contaminant of acids, alkalis or metals, there is a risk of accidental production of arsine when such acids or alkalis interact with a metal. Zinc often contains enough arsenic to create a hazard when it reacts with an acid or alkali. Commercial sulphuric acid, made by the chamber process, contains 0.2 to 0.3 per cent arsenic, which can settle out on standing to form deposits in the acid storage tank. These deposits contain up to 45 per cent arsenic, calculated as As_2O_3 .

Other reported sources of arsine exposure include:

- in certain circumstances, spraying water on slag to reduce dust or to dissolve out soluble residues;
- using galvanised buckets to remove sludge from tanks;
- adding powdered zinc to an acidified liquor obtained from smelter flue dust to reclaim cadmium;
- using phosphoric acid to clean an aluminium tank which is contaminated by sodium arsenite;
- using an aluminium ladder to descend into a tank containing sodium arsenite. (The aluminium ladder reacted with the sodium arsenite, liberating arsine.);

- pouring freshly diluted commercial hydrochloric acid containing sodium arsenite through the pipes of a water jacket. (The mixture of water and sodium arsenite under these conditions led to the generation of arsine.);
- cleaning out a sheep dipping vat previously contaminated with arsenical insecticide and subsequently used to contain another insecticide to which superphosphate had been added. (An acid medium led to arsine production.);
- using a commercial drain cleaner to clean a drain containing arsenical residues. (The drain cleaner contained sodium hydroxide, sodium nitrate and aluminium chips, which in turn bonded with the arsenic and produced arsine.); and
- filling balloons with hydrogen generated by the reaction between hydrochloric acid and zinc contaminated with small amounts of arsenic.

Appendix 2

Metabolism and excretion of arsenic and biological monitoring

Metabolism and excretion

Absorbed arsenic is rapidly eliminated through the kidney either unchanged or as cacodylic acid and methylarsonic acid. Inorganic arsenic is excreted unchanged in the urine during the first hours after the start of exposure. After about eight hours most of the excreted arsenic is as cacodylic acid and methylarsonic acid.

About three-quarters of a single dose of trivalent inorganic arsenic is eliminated within a few days or, at most, within a week, with the remainder being dispersed in the tissues. In the skin, brain and skeleton the concentrations decrease rather slowly. The health effects after long term exposure to arsenic are possibly just as much a result of continuous exposure to excessive amounts of arsenic as they are of accumulation of arsenic.

Biological monitoring

Biological indicators of arsenic are urine, blood, hair and nail. Of these indicators, urine arsenic is the best indicator of current or recent exposure.

Urine

The currently chosen method for biological monitoring of workers exposed to inorganic arsenic is the determination of the sum of inorganic arsenic, monomethylarsonic acid and cacodylic acid in the urine. Seafood provides an additional source of arsenic which may cause elevated arsenic levels for 1-2 days.

A urine sample taken over 24 hours should be used for analysis. Absorption of arsenic compounds is reflected in urine within 24 hours. However, the clearance of arsenic from the body is very rapid and urine concentrations are very time dependant.

It has been estimated that an airborne exposure standard of 50 μg inorganic arsenic/ m^3 would lead to an average urinary excretion of 220 μg of arsenic, determined by the above method, per gram of creatinine where urine is collected at the end of a shift after a few days of exposure. Levels in excess of 0.15 mg/L as arsenic indicates excessive exposure (in the absence of other sources).

Blood

Because of the short half-life of arsenic, blood level readings are only useful within a few days of acute exposure and are not useful to assess chronic exposure.

Hair and nail

Arsenic in hair and nail is a good indicator of the amount of inorganic arsenic absorbed during their growth period. However, as there is no reliable method which will distinguish external contamination by arsenic from arsenic that has been absorbed and metabolised in the body, the estimation of arsenic in hair and nail is not recommended for monitoring occupational exposure. This method is necessary, however, for assessing past exposure.

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